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Permittivity Properties of Nickel Zinc Ferrite-Oil Palm Empty Fruit Bunch-Polycaprolactone Composite

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Abstract

The dielectric properties of composites based on nickel-zinc-ferrite (NZF) filler can be improved by the addition of various types of materials. Amongst others, ferrite–polymer composites have been subjected to wide range of research, due to their extensive applications: electromagnetic interference shielding, microwave absorption, electrodes and sensors. In this study, $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (NZF) was prepared via conventional solid-state method. While NZF–OPEFB-PCL composite has been prepared via the mechanical milling mode and then characterized by X-ray powder diffraction. Dielectric properties of the composite, such as dielectric constant, loss factor and loss tangent were measured at different filler percentage over a wide range of frequency (0.20MHz-20GHz). An open ended coaxial probe connected to a vector network analyzer (VNA) was utilized for the evaluation of dielectric properties for materials and composites under test at the room temperature. Both dielectric constant and loss factor values increased due to the filler increment in the polymer matrix, where the composition of 15% NZF gives the extreme permittivity value at the used microwave frequency. Furthermore, the obtained results confirmed that dielectric properties of the composite can be controlled by the proper loading and the wise filler choosing. The adjusted properties support the purpose of polymer composite materials for microwave and communicational applications.

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Keywords: Oil palm fibre, polycaprolactone, ferrite, polymer composite, dielectric properties.

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1. Introduction

One of most important feature of magnetic polymer composites is the flexibility of their properties which can be fit to the exaction of particular applications. NZF is a significant member in the class of general ferrites due to their diverse properties. For example they exhibit a wide range of permeability, coercive force and magnetic and electric loss[1]. While ferrite-fibre-polymer composites have several pros such as; easy fabrication into complex shapes, resilience with the required mechanical strength, cheap, stable, and has a wide range of technological applications where numerous magnetic and electrical properties can be observed based on the composition[2]. Scientists and engineers paid a great attention to magnetic polymer composites, where they find scope for possible exploitation of commercial applications in various fields such as electromagnetic interference (EMI) shielding, electrodes and sensors, and microwave absorption[3]. NiZn-ferrite is one of the most versatile magnetic material which comes under a group of technologically important magnetic materials based on their distinctive properties such as stability, very good dielectric material, electrical resistivity, low dielectric loss chemical stability and others which play important roles in the scientific and industrial sectors[4]. Thus, such composites have extensive applications in microwave devices and core materials for power transformers in electronics and telecommunication[5]. Both electrical and magnetic properties of NZF-materials are strongly depending on the purity of ferrite powder, its microstructure, grain boundary and the chemistry preparation[6].

The ring-opening polymerization of ε-caprolactone provides a semi-crystalline PCL-polymer of -60°C glass temperature with low melting point ranged in between 30-70°C based on its molecular weight. This low melting point and special blend-compatibility has encouraged extensive research of attractive applications in various fields[7]. Among the other natural fibres, oil palm empty fruit bunch (OPEFB) fibre is very common in Malaysia. The OPEFB is a solid waste product of the oil palm milling process, extracted by the retting process of the empty fruit bunch and has a high moisture content of approximately 55–65% and high silica content of about 25% of the OPEFB. Average yield of OPEFB fibre is about 400 g per bunch. Mesocarp fibres are left as a waste material after the oil extraction which have less effect on the environment[8].

The topic of the current study includes the preparation of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ then its incorporation in an oil palm empty fruit bunch these materials reinforced polycaprolactone matrix for the modification of dielectric properties of the resulted composite. An open ended coaxial probe method was utilized for the evaluation of the dielectric properties for materials and composites under test. The structural characterization of NZF using X-ray diffraction (XRD) was also reported. The effect of filler loading on dielectric properties of these composites was studied as well, where these composites can be used as potential microwave absorbers through a wide range of frequencies. With the visualization to understand the dielectric development in NZF-OPEFB-PCL composite, a study on the dielectric properties of NZF, pure OPEFB, pure PCL and different compositions of NZF-OPEFN-PCL composites were also tackled. The relative complex permittivity is given by

$$\varepsilon_r = \varepsilon' - j\varepsilon'' \qquad (1)$$

Where ε' is the dielectric constant and ε'' is the loss factor. While the total dielectric loss tangent (tan δ) is given by

$$\tan\delta = \varepsilon'' / \varepsilon' \qquad (2)$$

Nomenclature

OPEFB	oil palm empty fruit bunch
PCL	polycaprolactone
NZF	nickel zinc ferrite
ε'	dielectric constant
ε''	loss factor
tan (δ)	loss tangent

2. Experimental details

NZF-filler of the composites was prepared via conventional solid state reaction method. Firstly, the preparing procedure for starting materials of NiO (99.7% purity), ZnO (99.9% purity) and Fe_2O_3 (99.7% purity) have been clearly specified according to the following stoichiometric equation[9]

$$x\,NiO + 1\text{-}x\,ZnO + Fe_2O_3 \longrightarrow Ni_x\,Zn_{1-x}\,Fe_2O_4 \qquad (3)$$

The dried powder is milled and pre-calcite in air at 900°C for 10 hours. Then it was grinded carefully to ensure homogeneity for the particles size of the powder.

The OPEFB-fibre used in this work was soaked in distilled water for 24 hours. Then the wet fibre is dried in an oven at about 80°C. This process was repeated twice. Later, the fibre is filtered and washed with acetone and dried again in the oven to remove the wax layer of the fibres. After that a grinded machine was utilized to grind fibre chains into small powder molecules that sieved carefully to 250µm sizes. The mixing process of NZF filler along with OPEFB-PCL was carried out in a Thermo Haake blending machine Poly drive three-phase motor with a drive of 1.5 kW, 3 · 230 V, 40 A with 50 min^{-1}speed. The total weight of the prepared sample for blending was 40 g. NZF and OPEFB/PCL were weighed according to the addition of filler percentage (2.5% - 15%). PCL-polymer was heated up to the melting point of 80°C and then both the fibre along with the ferrite particles were added and mixed together for 20 minutes to get homogeneous composites. After that, the composite was fabricated using rectangular mould affected by hot and cold pressed for 10 minutes each to get a substrate of 10 mm thickness. All the samples were examined by XRD to determine the microstructure and purity of the samples. An open ended coaxial probe in conjunction with a VNA at (0.20MHz-20GHz) rang of frequency was utilized for the dielectric examination.

3. Results and discussion

Fig. 1 showed the XRD patterns for $Ni_{0.5}Zn_{0.5}Fe_2O_4$,it is clearly observed that all the diffraction main peaks for NZF were at 110, 220, 311, 222, 400, 422, 511 and 440, with the related scattering angle at 2θ= (24.18º), (31.80º), (33.12º), (34.51º), (40.98º), (49.39º), (54.30º) and (64.18º), respectively. The XRD patterns of NZF particles are nearly matched with the referenced patterns (JCPDS 01-072-6799), which exhibit the typical spinal structure. The unnecessary peaks in the Fig. could be corresponding to nickel oxide molecules that were not perfectly crystallized to the NZF structure. While, the XRD patterns of NZF/PCL/OPEFB composites at different compositions were also presented in Fig. 1. For this composite, the NZF is the filler while OPEFB-PCL represents the host which has a semi crystalline structure. All the peaks shown in the profile belong to the three main materials used for our composites preparation. The intensity of the peak located at 36° increased due to the filler percentage increments, which is non-existent for the PCL-OPEFB host materials. Whereas, new peaks located at the 18° and 30° began to appear as the filler addition increased up to 15% which indicates the strong interaction has been taking place between the filler with the host material.

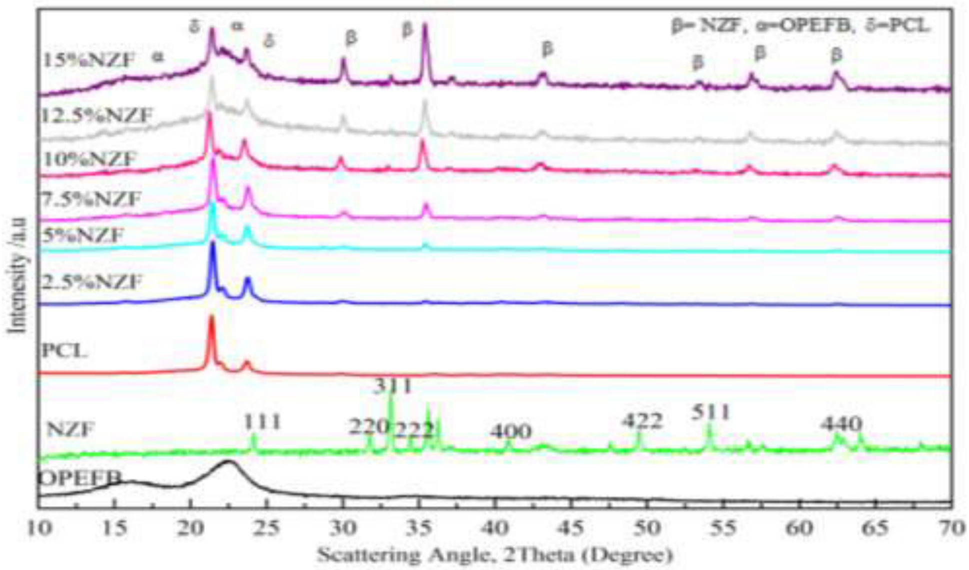

Fig. 1. XRD patterns of $Ni_{0.5}Zn_{0.5}Fe_2O_4$/PCL/OPEFB microcomposites at different compositions

4. Dielectric characterization

Fig. 2 shows the variation of ε' versus frequency at (0.20MHz-20GHz) for NZF/OPEFB/PCL composites at the room temperature. It can be seen from the figure that ε' decreased as the frequency increased. Such reduction in dielectric values is a normal behaviour in the case of Ni–Zn mixture of spinal ferrites which can be explained based on Koop's phenomenological theory[10]. The theory has considered the dielectric structure as an inhomogeneous medium of two layers of Maxwell–Wagner type. The minimum dielectric constant is displayed by the pure PCL-polymer, while the maximum value belongs to the pure filler. It can be concluded that the higher dielectric constant of 15%NZF filler can be proposed to obtain the highest dielectric value of (5.459) at 0.2MHz when added to the OPEFB-PCL host composite, which is more distinct at low frequencies. The dielectric properties of the material depend upon the polarizability of the molecules[11]. The polarizability of non polar molecules emerges from two factors; electronic and atomic polarization. The orientation polarization represents the third factor for polar molecules where the application of applied electric field causes an orientation of matters. Thus, the composite polarizability is the sum of electronic, atomic and orientation polarization which increase the dielectric constant values. Hence the dielectric constant increases with fibre loading increments at all frequencies, while the decrease shown at high frequencies is referred to the reduction in orientation polarization. At low frequencies, complete orientation of the molecule is possible while at medium frequencies there is only a little time for orientation. Orientation of the molecules is not possible at all at very high frequencies.

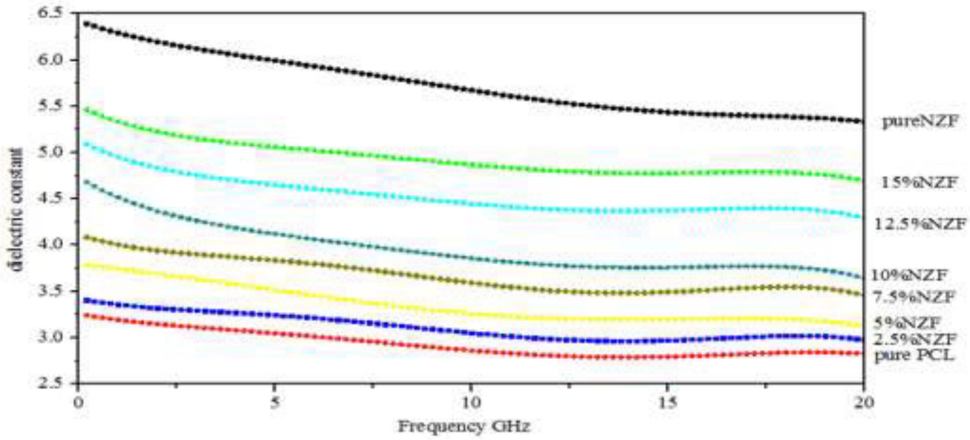

Fig. 2. The dielectric constant vs frequency of $Ni_{0.5}Zn_{0.5}Fe_2O_4$/PCL/OPEFB microcomposite at different filler percentages

Fig. 3 shows that the dielectric loss factor at all frequency range decreased gradually due to the free charge motion within the material. It shows the imaginary part vs frequency for the matrix, filler and the composite at different filler percentages.

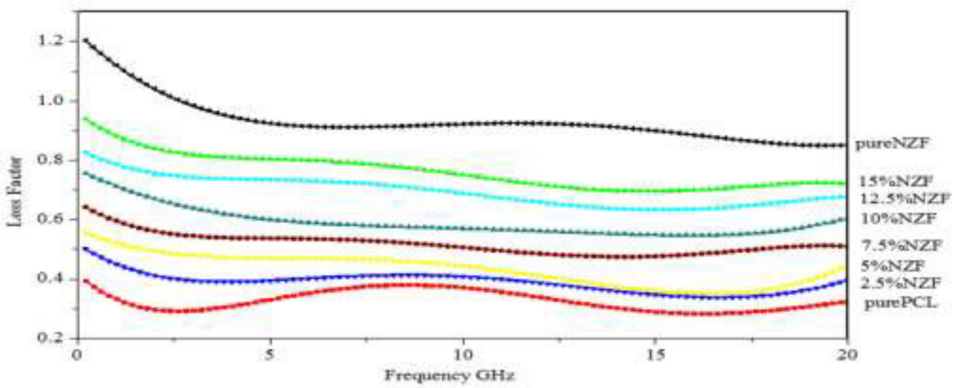

Fig. 3. Loss factor vs frequency of NZF/PCL/OPEFB composite for different doped filler percentages

The loss tangent value is defined as the tangent of the angle (δ) between the amplitude vectors of the total and charging currents[12]. Fig. 4 presents the loss tangent results as well as the calculated loss tangent values based on Eq. (2), where the frequency relay on tan (δ) values of the NZF-filler at (0.20Hz to 20 GHz) frequency range. Loss tangent of all composites shows similar unordered behaviour of samples due to jumped frequencies and the re-arrangement of composite particles. The highest loss tangent was captured at lowest frequency values.

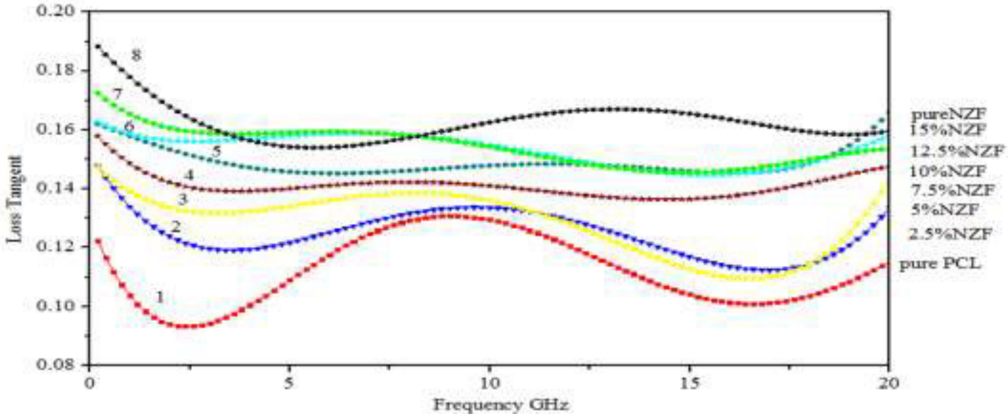

Fig. 4. Loss tangent vs frequency for NZF/PCL/OPEFB composite at different doped filler percentages

Fig. 5 (a and b) in conjunction with Table 1 present the variation of ε' and ε'' with loading weight percentage of NZF filler in the composition at random frequencies (0.20Hz, 5GHz, 10 GHz and 20GHz). The effective medium theory is clearly explained the increment of dielectric constant and loss factor values in accordance to the loading filler addition[13], where a higher dielectric constant of the polymer-based composite can be obtained by adding high dielectric constant filler into the low dielectric constant polymer matrices and vice versa. The dielectric constant and loss factor at (0.20MHz) are the highest compared with other frequencies (5, 10, 15 and 20) GHz. This behaviour is caused by the movement of portable chargers at low frequency which is unstable and reflects dielectric loss.

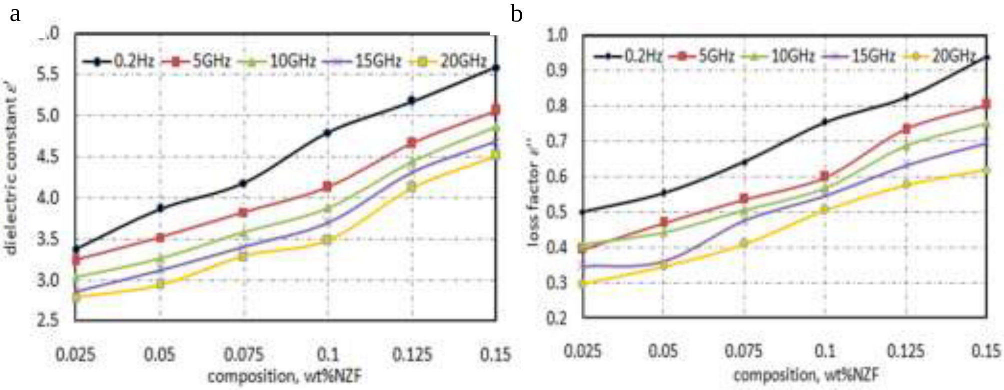

Fig. 5. (a) Variation of dielectric constant with respect to NZF% of the composite. (b) Variation of dielectric loss factor with respect to NZF% of the composite

Fig. 6 along with Table 2 present the variation of tan (δ) with different loading percentages of the filler along with OPEFB reinforcement PCL at unassigned frequencies such as 0.20MHz, 5GHz, 10GHz and 20GHz. Unsteady increment of the loss tangent was recognized due to the NZF-filler loading addition.

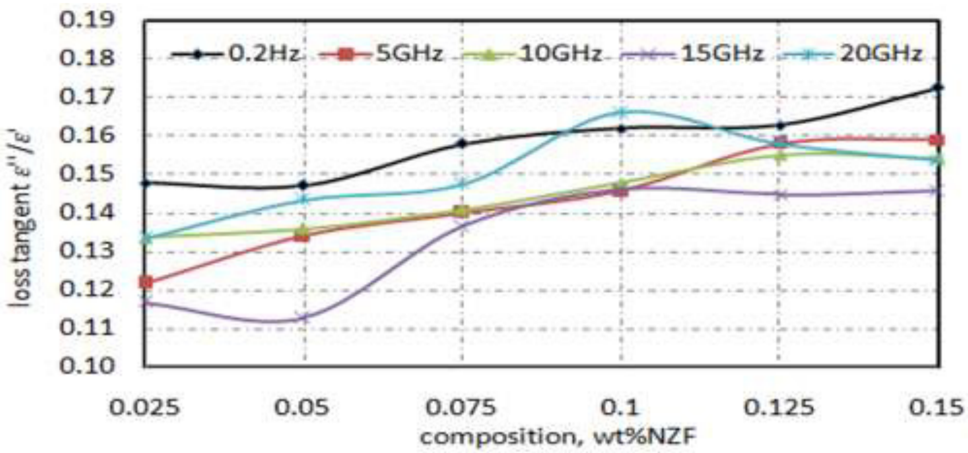

Fig. 6. Variation of dielectric loss tangent with respect to NZF% in the composite

Table 1. Variations of the dielectric constant and loss factor values with respect to the composition

Wt% NZF	Dielectric Constant ε'					Loss Factor ε''				
	0.2Hz	5GHz	10GHz	15GHz	20GHz	0.2Hz	5GHz	10GHz	15GHz	20GHz
0.025	3.369	3.240	3.040	2.865	2.790	0.502	0.395	0.408	0.347	0.297
0.05	3.867	3.518	3.268	3.121	2.939	0.556	0.471	0.444	0.360	0.348
0.075	4.182	3.827	3.581	3.403	3.293	0.643	0.537	0.507	0.477	0.410
0.1	4.795	4.128	3.883	3.700	3.482	0.756	0.600	0.570	0.549	0.506
0.125	5.174	4.662	4.444	4.307	4.128	0.826	0.734	0.689	0.633	0.578
0.15	5.592	5.059	4.866	4.685	4.513	0.939	0.804	0.751	0.695	0.620

Table 2. The variance in loss tangent values of different NZF filler percentage at random frequencies

Wt% NZF	Loss Tangent $\varepsilon''/\varepsilon'$				
	0.2Hz	5GHz	10GHz	15GHz	20GHz
0.025	0.148	0.122	0.134	0.117	0.133
0.05	0.147	0.134	0.136	0.113	0.143
0.075	0.158	0.140	0.141	0.137	0.148
0.1	0.162	0.146	0.148	0.146	0.166
0.125	0.163	0.158	0.155	0.145	0.158
0.15	0.173	0.159	0.154	0.146	0.154

5. Conclusion

The knowledge in materials behaviour is requisite to understand the potential use of these materials in a wide range of microwave applications. $Ni_{0.5}Zn_{0.5}Fe_2O_4$ of high purity was successfully prepared by using the solid state method. The melt blend technique was conveniently utilized for the preparation of NZF-OPEFB-PCL composites via the Thermo Haake machine. In this work, the effect of ferrite filler particles on the dielectric phenomena of NZF-OPEFB-PCL composites was measured by using an open ended coaxial probe. The obtained results of both dielectric constant and loss factor measurement revealed the proportional relation with the NZF filler loading in the composite, but they react inversely with the frequency increments for all samples under test. Obviously, the $Ni_{0.5}Zn_{0.5}Fe_2O_4$–PCL-OPEFB composite of 15% filler composition showed the highest dielectric constant, loss factor and loss tangent level. Thus, it is revealed that the increase of the filler amount in the matrix has successfully increased the dielectric polarization of the composite.

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